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Screening of low-cost materials as heterogeneous catalysts for olive mill wastewater Fenton's peroxidation

E. Domingues[a],*, F. Rodrigues[a], J. Gomes[a], M.J. Quina[a], S. Castro-Silva[b], R.C. Martins[a],*

[a] *University of Coimbra, CIEPQPF – Chemical Engineering Processes and Forest Products Research Center, Department of Chemical Engineering, Faculty of Sciences and Technology, Rua Sílvio Lima, 3030-790 Coimbra, Portugal*
[b] *Adventech – Advanced Environmental Technologies, Rua de Fundões 151, 3700-121, São João da Madeira, Portugal*

Abstract

Olive mill wastewater (OMW) is a complex effluent, with a high organic load and toxic compounds. Its seasonal production is an added difficulty for treatment systems. In this work, the heterogeneous Fenton process is used with low-cost catalysts, that are wastes rich in iron and other materials naturally present in nature, namely Red Mud (RM), the volcanic rocks of the Azores (VRA) and the volcanic rocks of the Canaries (VRC), to treat a mixture of five phenolic compounds usually present in OMW (3,4 - Dihydroxybenzoic, 4 - Hydroxybenzoic, 3,4 - Dimethoxybenzoic, 3,4,5 - Trimethoxybenzoic and Trans-cinnamic acids). The effect of adding hydrogen peroxide stepwise was also investigated and it was found that adding the oxidant at once is more efficient than the staged addition, for removing phenols as well as leading to less residual hydrogen peroxide. With regard to the utilization of low-cost catalysts, it was concluded that at the end of 60 min and for a concentration of 1 g/L of catalyst, the removal of phenolic content reaches 100% for RM, while in the case of VRA and VRC this value is 72.0% and 74.6%, respectively.

1. Introduction

Olive mill wastewater (OMW) needs attention due to its significant impacts on the environment. Considering that about 30 million m^3 of OMW are generated annually worldwide, only $1/4$ of this has received appropriate treatment [1]. The impacts on the environment are significant, essentially due to its acidic properties, the high organic load (COD can reach values above 170 g O$_2$/L, containing phenolic compounds above 24 g/L and long

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* Corresponding authors.
   E-mail addresses: evadomingues@eq.uc.pt (E. Domingues), martins@eq.uc.pt (R.C. Martins).

chains fatty acids) [2]. Based on these properties and recalling that it is a seasonal effluent, when stored, oxidation and polymerization reactions (tannic acid, lignin) may occur, resulting in recalcitrant compounds, giving it a dark color and bad odors. Moreover, its low BOD_5 to COD ratios make these streams resistant to biodegradation and, consequently, cannot be sent to treatment plants based on biological processes [3]. There are physical and thermal processes that are useful as a pre-treatment to remove suspended solids and to decrease volume. However, they are not efficient due to the high operational costs associated (especially energetic), nor do they contribute to the depollution of toxic compounds present in it. As an alternative, other treatments emerge. According to Rahmanian et al. [4], physical–chemical treatments (neutralization, precipitation, etc.) are cheaper treatment routes, but require the integration of later treatment, which increases the processing time. On the other hand, advanced oxidation processes (AOP) show to be more effective in pollutant degradation despite the higher costs. Thus, considering the large organic load of the oil mill effluents as well as the presence of phenolic compounds, it is necessary to reach the legal limits for the management of these residues, and the option under study is the Fenton reaction. In this case, the literature has highlighted the possibility of achieving degradation of phenolic compounds using low-cost catalysts. The Fenton process is efficient under ambient conditions (pressure and temperature) which reduces the process energetic demands, the reaction time is relatively short compared to other existing processes, the reagents do not present any danger to the user or require the application of specific equipment [5]. Regarding the degradation of organic compounds, it is a promising technique, through the partial oxidation of phenolic compounds, resulting in a decrease in COD. The efficiency of the reaction is essentially dependent on certain parameters such as the pH of the medium (values between 2.5 and 4.5), and the oxidant/catalyst ratio (H_2O_2/Fe^{2+}), which is important to optimize the quantities of reagents to obtain the highest degree of degradability and a smaller amount of residual H_2O_2 [6]. As an alternative to the homogeneous systems, there is the possibility of carrying out the reaction using a solid catalyst (heterogeneous process) that remains in suspension at the end. In this way, there is no longer a limitation for the removal of solubilized iron, mediated by additional separation processes and, therefore, it becomes a less complex operation [7]. In this method, the solid catalyst must be rich in iron or other materials with similar catalytic properties, to promote the oxidative activity of H_2O_2 (via hydroxyl radicals) to degrade each organic pollutant. In this work, the behavior of the Fenton reaction with the use of catalysts such as RM, VRC and VRA will be studied. According to the studies presented by Domingues et al. [8] and Martins et al. [9], these have high iron content and not needing modifications, showing a priori materials with the potential to be applied in the Fenton process. Thus, the focus is given to concepts such as environmental impact and circular economy, based on the use of waste from the metallurgical industry and availability in nature, as a catalyst.

2. Materials and methods

2.1. Catalysts and reagents

RM was provided by a Greek aluminum producer, was washed with water, dried at 105 °C for 24 h, and ground until a powder was obtained. RM was previously characterized by Domingues et al. [8]. VRC and VRA were collected from Canaries and Azores Island and were characterized in the works [9,10]. Hydrogen peroxide (33% w/V) was purchased from Panreac.

The synthetic OMW initial concentration was obtained through the mixture of 100 mg/L of each phenolic acid (3,4 - Dihydroxybenzoic, 4 - Hydroxybenzoic, 3,4 - Dimethoxybenzoic, 3,4,5 - Trimethoxybenzoic and (5) Trans-cinnamic).

2.2. Experimental procedure

Fenton's reactions were carried out in a batch spherical reactor, under ambient temperature and pressure conditions, the pH of the medium was readjusted to 3.0, and the reaction was carried out for 60 min. A catalyst load of 1 g/L and an amount of oxidizer (H_2O_2) of 100 mg/L were applied. The oxidant was fully introduced at the beginning of the reaction or in several aliquots over time. The reactor was agitated with magnetic stirring at 300 rpm. The required amount of catalyst is added 10 min before starting the experiments to test the adsorption of the pollutants. In the Fenton experiments, the reaction started when H_2O_2 was introduced. Samples taken periodically were filtered using 1 µm glass fiber membranes to remove the catalyst particles and then a few drops of $Na_2S_2O_3$ (0.1 N) were added to remove the remaining H_2O_2, stopping the reaction.

2.3. Analytical techniques

The concentration of the individual phenolic acids was obtained by HPLC (Shimadzu) analysis using a C18 (SiliaChrom) column at 40 °C. The mobile phase (0.5 mL/min) consists of a 50:50 mixture of methanol and acidified water (0.1% orthophosphoric acid). The determination occurred at 255 nm.

The phenolic content of the effluent was determined by the Folin–Ciocalteau method and, since the calibration curve was based upon standard solutions of gallic acid, the polyphenolic content (TPh) was expressed as mg/L of equivalent gallic acid. The detailed procedure is described elsewhere [11].

Hydrogen peroxide concentration along the reaction was followed spectrophotometrically (PG Instruments T60 spectrophotometer) using the potassium titanium (IV) method.

3. Results and discussion

3.1. Catalysts characterization

In the heterogeneous Fenton process, three solid catalysts were used, namely RM, VRA, and VRC. These materials are attractive due to their physical and chemical properties, the high iron content, and because it is possible to be used as solid catalysts. In this way, they have the potential to be used in the Fenton process, avoiding the application of a homogeneous catalyst that requires a subsequent separation stage. On the other hand, these materials can be considered low-cost catalysts, since come from industrial residues, from which they can be reused and reintegrated in other process cycles (in the case of RM) or reused in nature, as in the case of VRA and VRC.

RM consists of elements such as Fe, Al, Ca, Ti, Si, and Na and is composed of significant fractions of Fe_2O_3 (hematite) and AlOOH (boehmite) [8]. The presence of hematite shows that RM is a source of Fe (III) and not of Fe (II).

The VRA composed mostly of Al, Fe, Ca, Mg, and O, accounts for a fraction of Fe in about 55.8% (w/w), which is higher than for the other elements. On the other hand, X-ray diffraction showed intense peaks corresponding to silicate compounds [10].

Concerning the VRC, from the study presented by Martins et al. [9], this solid catalyst presents traces of elements such as Fe, Na, Ca, Mg, while the former represents the highest fraction (6.45%). In this case, complexes such as hematite, pyroxene (single chain inosilicates), quartz, and feldspar were detected.

Another relevant characteristic regarding catalytic materials is related to its specific area (or BET surface area) since it determines the area available for the reactions to occur. According to the literature, these materials register the values of 0.6, 28.3, and 3.59 m^2/g, for RM, VRA, and VRC, respectively.

3.2. Effect of [H_2O_2] injection mode

The optimization of H_2O_2 charge is key due to the potential scavenging effect of this reagent when in excess [12]. One way to control this parameter may be to gradually introduce it in the reaction medium. The catalyst used to perform these tests was RM, based in the conditions optimized previously (pH = 3.0, [H_2O_2] = 100 mg/L and [catalyst] = 1 g/L) [8]. In all tests, except the first in which the amount of total hydrogen peroxide is injected, half the amount of oxidant is injected at the initial moment (t = 0 min) and then the other half is divided according to the number of injections (totality at 0 min for 1x; at 15 and 30 min for 2x; at 10, 15 and 30 min for 3x; and at 5, 10, 15 and 30 min in the case of 4x) (Fig. 1a).

Fig. 1b shows the effect of the hydrogen peroxide injection mode on the removal of phenolic compounds present in the simulated effluent, measured by the Folin–Ciocalteau method (in the form of total phenolic content). Fig. 1a there is less residual H_2O_2 amount when H_2O_2 (100 mg/L) is totally injected at the beginning of the reaction. This behavior is possibly due to its rate of decomposition (which is proportional to the amount of reagent) being higher at the beginning of the reaction than during the process. However, there are inconstant moments in the amount of residual H_2O_2, suggesting that it is consumed and formed during the reaction. In fact, studies show that oxidation reactions involving unsaturated carbon bonds can lead to the formation of H_2O_2. This fact was verified by Martins et al. [13] in the case of ozonation, with the possibility of such a process also occurring in the case of the Fenton reaction. It is also verified, when comparing the profile of one injection (1x) with the profile of 2x, 3x, and 4x injections, that in these cases there are higher residual oxidant values. This suggests that the addition spread over
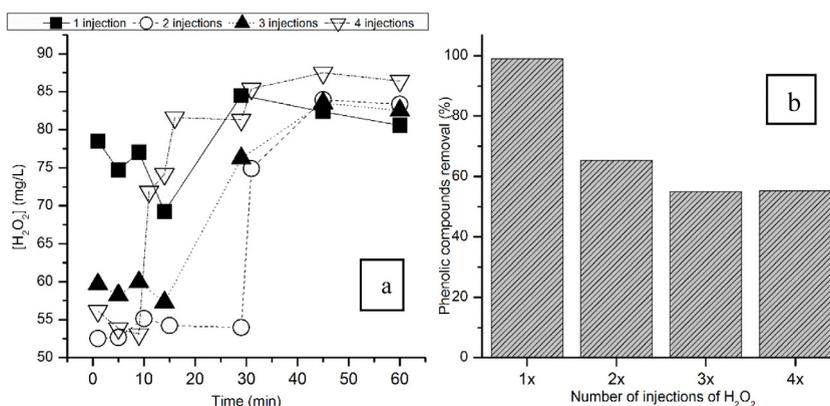
Fig. 1. (a) Evolution of residual hydrogen peroxide, with different injections, over 60 min of reaction (b) Total degradation of phenolic content.

the process leads to the accumulation of H_2O_2, affecting efficiency. The results in Fig. 1b show that for only a single injection of H_2O_2 (at the beginning of the reaction), there is a higher removal of phenolic compounds (100%) present in the simulated effluent. On the other hand, in the case in which 3 and 4 injections are performed, the lowest value is reached in the phenolic content removal (approximately 55%) after 60 min of reaction. The kinetics of removal is higher at the beginning of the process, hence there are higher rates of removal with just one injection. In a more detailed analysis, phenolic acids were individually identified and quantified through HPLC analysis.

In Fig. 2, the final removal of each phenolic acid present in the simulated effluent is observed when hydrogen peroxide was introduced in different injections.
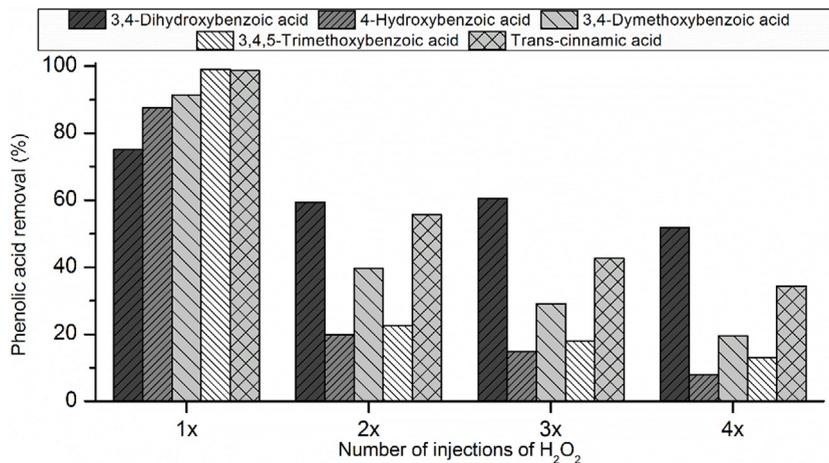
Fig. 2. Degradation of phenolic acids, for the different injections of H_2O_2, with $[H_2O_2] = 100$ mg/L, pH = 3.0, $[Fe^{2+}] = 1$ g/L.

HPLC analyzes show higher degradation rates of phenolic acids when H_2O_2 is fully injected at the beginning of the reaction, corroborating the conclusions obtained when the total phenolic content was measured. More specifically, after 60 min, removals of 75.1% of 3,4-dihydroxybenzoic acid, 87.6% of 4-hydroxybenzoic acid, 91.4% of 3,4-dimethoxybenzoic acid, 99.1% of 3,4,5-trimethoxybenzoic acid and 98.7% trans-cinnamic acid were obtained. Therefore, it is possible to state that the total injection at the beginning of the reaction shows more promising results. It should be noted that, in general, the acid that achieves the greatest degradation is trans-cinnamic acid while the most difficult to remove is 4-hydroxybenzoic acid. In fact, while the first has a very reactive double bond outside the benzene ring in its ortho position, the second has only one –OH functional group, which makes it less apt to be attacked by hydroxyl radicals. Hydroxyl radicals have an electrophilic character and therefore are more prone to

attack an isolated oleophilic (unsaturated) double bond in the benzenic ring. This explains the greater degradation typically achieved by trans-cinnamic acid. As previously mentioned, the molecular structure of the 4-hydroxybenzoic compound, has only one functional group –OH in the 4th position of the benzene ring. In this way, this represents a limitation to the electrophilic attack by the hydroxyl radicals since they are more preferred by the 3rd positions during the oxidation process.

3.3. Screening of low-cost catalysts

The cost of the catalyst is also an important variable in the economy of a process. In this sense, the application of natural materials or residues from other processes can be interesting alternatives to industrially synthesized catalysts. In fact, the production of catalysts entails large energetic costs associated to drying and calcination of the materials. In this sense, a residue RM and two types of volcanic stones were selected: VRA and VRC.

It is also relevant to evaluate the efficiency of the process in removing phenolic content and organic matter using VRA and VRC compared to RM. According to the previous results, it was decided to make only one injection of hydrogen peroxide (at the beginning of the reaction). All catalysts were tested using a load of 1 g/L.

Fig. 3a shows the comparison of the performance of the different catalysts in the Fenton reaction with respect to the evolution of the amount of residual hydrogen peroxide. Fig. 3b compares the removal of the total phenolic content after 60 min of Fenton's reaction using the different catalysts.
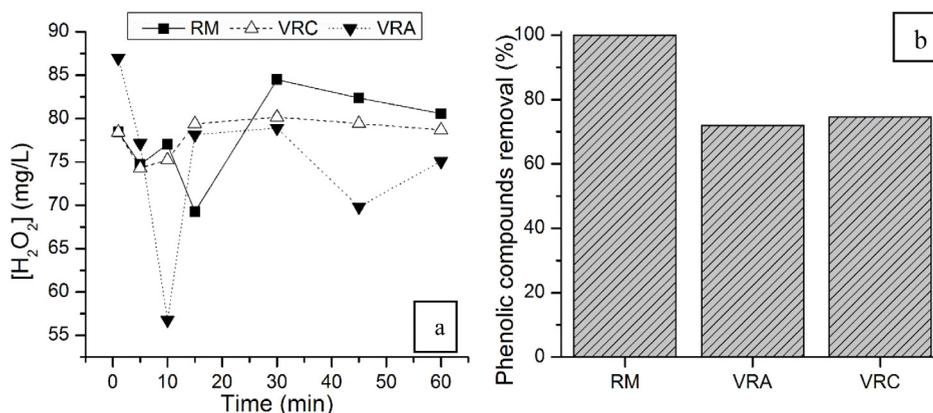
Fig. 3. (a) Evolution of the residual amount of H_2O_2, over time, for RM, VRA and VRC. (b) Degradation of phenolic content, for RM, VRA and VRC, for pH = 3.0, [Catalyst] = 1 g/L and [H_2O_2] = 100 mg/L.

The amount of residual H_2O_2 is less when using the VRA, and in the first 10 min of reaction, the consumption of H_2O_2 is highest. This can be explained by the larger BET surface area and, thus, greater availability of active sites on the catalyst surface. This phenomenon is reflected in a higher rate of decomposition of hydrogen peroxide in hydroxyl radicals or in species with less oxidative power (for example, hydroperoxyl radicals - HO_2). RM, on the other hand, shows fluctuations over time, but less abrupt consumption of hydrogen peroxide than VRA. At the end of 60 min, it ends with a higher residual amount compared to the other catalysts. As previously mentioned, it has a smaller BET surface area, which is proportional to the number of active sites available for H_2O_2 decomposition. Comparing the residual H_2O_2 profile over the reaction time for the 3 catalysts, with S_{BET}, it is possible to affirm a relationship between this parameter and the residual amount of oxidant, that is, the higher this value, the lower the residual amount obtained.

Despite differences in the evolution of the amount of residual hydrogen peroxide using the various catalysts (Fig. 3a), this is not evident regarding the removal of the phenolic content. In fact, there are significant differences between the efficiencies achieved when each of the three catalysts is used. At the end of 60 min, the removal of phenolic content reaches 100% for RM, while in the case of VRA and VRC this value is 72.0% and 74.6%, respectively (Fig. 3b). Unlike Gomes et al. [10], the increase in the BET surface area of the catalyst was not directly related to the degradation rate of phenolic compounds, since in this case the solid with the lowest BET area value (RM) has better removal efficiencies. Possibly these materials promote the decomposition of hydrogen peroxide in

species with less oxidative power, influencing the degradation capacity of organic carbon. This behavior is suggested in the studies by Martins et al. [13], observing lower performances when using VRC stone when compared to the non-catalytic ozone process.

4. Conclusion

In this work, a synthetic OMW was studied based on five phenolic acids usually present in the real OMW (3,4 - Dihydroxybenzoic, 4 - Hydroxybenzoic, 3,4 - Dimethoxybenzoic, 3,4,5 - Trimethoxybenzoic, and (5) Trans-cinnamic). This effluent was treated by the Fenton process using three low-cost catalysts: RM, VRA, and VRC. It was concluded that:

-At the end of 60 min the removal of phenolic content reaches 100% for RM, while in the case of VRA and VRC this value is 72.0% and 74.6%, respectively;

-The 3 catalysts show a shifting behavior, revealing that there is formation and decomposition of H_2O_2 throughout the process.

-The degradation rate of phenolic compounds was not directly related to the increase in the BET surface area of the catalyst.

The study of the effect of hydrogen peroxide injection mode was also evaluated using RM in the following conditions: pH = 3.0, $[H_2O_2]$ = 100 mg/L and [catalyst] = 1 g/L). It was concluded that less residual oxidant amount is obtained when the totality of H_2O_2 (100 mg/L) is injected at the beginning of the reaction, while a greater removal of phenolic compounds (100%) was observed in this case.

The use of wastes and/or natural materials avoids the need for synthesizing catalysts that entails larger energetic costs related with the thermic treatment of such materials. Thus, globally the wastewater treatment cost will decrease while contributing to a circular economy.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

References

[1] McNamara CJ, Anastasiou CC, O'Flaherty V, Mitchell R. Bioremediation of Olive mill wastewater. Int Biodeterioration Biodegrad 2008;61:127–34. http://dx.doi.org/10.1016/j.ibiod.2007.11.003.

[2] Chatzisymeon E, Foteinis S, Mantzavinos D, Tsoutsos T. Life cycle assessment of advanced oxidation processes for Olive mill wastewater treatment. J Cleaner Prod 2013;54:229–34. http://dx.doi.org/10.1016/j.jclepro.2013.05.013.

[3] Martins RC, Quinta-Ferreira RM. A review on the applications of ozonation for the treatment of real agro-industrial wastewaters. Ozone Sci Eng 2014;36:3–35. http://dx.doi.org/10.1080/01919512.2013.842158.

[4] Rahmanian N, Jafari SM, Galanakis CM. Recovery and removal of phenolic compounds from Olive mill wastewater. J Am Oil Chem Soc 2014;91:1–18. http://dx.doi.org/10.1007/s11746-013-2350-9.

[5] Domingues E, Gomes J, Quina MJ, Quinta-Ferreira R, Martins R. Detoxification of Olive mill wastewaters by Fenton's process. Catalysts 2018;8. http://dx.doi.org/10.3390/catal8120662.

[6] Peres JA, Beltrán De Heredia J, Domínguez JR. Integrated Fenton's reagent - coagulation/flocculation process for the treatment of cork processing wastewaters. J Hazard Mater 2004;107:115–21. http://dx.doi.org/10.1016/j.jhazmat.2003.09.012.

[7] A.F. Rossi, Martins RC, Quinta-Ferreira RM. Composition effect of iron-copper composite catalysts in the Fenton heterogeneous process efficiency and cooxidation synergy assessment. Ind Eng Chem Res 2014;53:15369–73. http://dx.doi.org/10.1021/ie501193x.

[8] Domingues E, Assunção N, Gomes J, Lopes DV, Frade JR, Quina MJ, et al. Catalytic efficiency of red mud for the degradation of Olive mill wastewater through heterogeneous Fenton's process. Water 2019;11. http://dx.doi.org/10.3390/w11061183.

[9] Martins RC, Henriques LR, Quinta-Ferreira RM. Catalytic activity of low-cost materials for pollutants abatement by Fenton's process. Chem Eng Sci 2013;100:225–33. http://dx.doi.org/10.1016/j.ces.2013.03.024.

[10] Gomes JF, Quinta-Ferreira ME, Costa R, Quinta-Ferreira RM, Martins RC. Paraben degradation using catalytic ozonation over volcanic rocks. Environ Sci Pollut Res 2018;25:7346–57. http://dx.doi.org/10.1007/s11356-017-1025-8.

[11] Martins RC, Leal HC, Quinta-Ferreira RM. Single and catalytic ozonation for phenolic wastewaters remediation current themes in engineering technology. 180. New York: Am. Inst. Phys.; 2008, p. 716–21. http://dx.doi.org/10.1063/1.2937615.

[12] Lucas MS, Peres JA. Removal of COD from Olive mill wastewater by Fenton's reagent: Kinetic study. J Hazard Mater 2009;168:1253–9. http://dx.doi.org/10.1016/j.jhazmat.2009.03.002.

[13] Martins RC, Ramos CM, Quinta-Ferreira RM. Low-cost catalysts to enhance ozone action on the depuration of olive mill wastewaters. Ind Eng Chem Res 2014;53:15357–68. http://dx.doi.org/10.1021/ie501187e.